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June 12, 1963

Mr. John J. Fackler
Contracting Officer
Space Electric Power Procurement Office
NASA, Lewis Research Center
21000 Brookpark Road
Cleveland 35, Ohio

Subject: Informal Monthly Report - Contract NAS3-2532

Dear Mr. Fackler:

In accordance with Article II-A of the subject contract, we are enclosing one copy of report GACD-4312 for the month of April 1963. By copies of this letter we are making other distribution of this report as required by the aforementioned contract article.

Very truly yours,

W. T. Kane
Contract Administration

WTK: ll

cc: NASA Program Manager, Code RN (1)
Donald Keaveney, WOO (1)
Office of Reliability & Quality Assurance (1)
John W. R. Creagh (5 + 1 repro)
John Keeler, WOO (1)
J. P. Cullinane, WOO (w/o attach)

GENERAL ATOMIC

Division of General Dynamics Corporation

John Jay Hopkins Laboratory
for Pure and Applied Science

GACD-4312

Copy No. 2

INVESTIGATIONS OF CARBIDES AS CATHODES FOR THERMIONIC SPACE REACTORS

Informal Monthly Report for the Period
April 1, 1963 through April 30, 1963

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Project No. 306
National Aeronautics and Space Administration
Contract No. NAS 3-2532

June 6, 1963

SUMMARY

The work carried out under Contract NAS 3-2532 during April, 1963, is summarized as follows:

1. Long-term Tests of the Vaporization and Emission of UC-ZrC and W-Clad UC in Cesium Vapor.

   1.1 Rate of Vaporization of UC-ZrC in Cesium Vapor.

   The two cells for the 1000-hr runs have been outgassed. The 30 UC - 70 ZrC and the 90 UC - 10 ZrC samples to be used for the study have been prepared. The rate of vaporization of the 30 UC - 70 ZrC sample in vacuum has been determined in order to establish the base-line data. The 90 UC - 10 ZrC sample is being outgassed.

   1.2 Emission Stability of UC-ZrC and W-Clad UC and UC-ZrC in Cesium Vapor.

   The second metallurgical life and performance test cell (MLP-B) containing a vapor-deposited W-clad UC emitter has been operated for a period of 110 hours. The test was terminated because a leak developed between the cell chamber and the electron-gun chamber. A control cell containing a solid W emitter is being assembled to check the modifications made in the design of the electron-gun chamber and filament. Components for four other life-test cells have been received. The UC - ZrC (90 UC - 10 ZrC and 30 UC - 70 ZrC) and the vapor-deposited W-clad 30 UC - 70 ZrC emitters are under preparation.

2. Studies of the High-Temperature Properties of UC - ZrC.

   2.1 Effect of Porosity on the Vaporization and Electron Emission Properties of UC - ZrC in Vacuum.

   Measurements have been made on the vacuum emission, chemical composition and open pore fraction of the cold-pressed and sintered nominal 30 UC - 70 ZrC sample B_1-9 whose vacuum rates of vaporization were determined during March, 1963. Measurements have also been made on the vacuum rates of vaporization of another cold-pressed and sintered nominal 30 UC - 70 ZrC sample B_1-9a obtained from the same

carbide piece as B_1-9.

2.2 Redeposition Studies.

Two 100-hr physical redeposition runs have been made between a UC cathode and a Ni anode in the all-metal redeposition cell to check the modified anode cooling device. The cell worked satisfactorily with the cathode at about 1800°C and the anode in the temperature range 285 to 750°C.

2.3 Thermionic Emission Microscopy.

The activation of the emission from a polished UC surface by thermal treatment in vacuum at various temperatures has been studied in the temperature range 1670 to 2000°K.

2.4 High-Temperature Mechanical Properties.

Calibration of the load train bellows and test of the alignment of the loading train have been made.

3. Irradiation Studies.

3.1 Unclad Carbide Capsule.

The irradiation of the unclad carbide capsule in GETR has proceeded satisfactorily during the second cycle.

3.2 Clad Capsule.

The cladding of the cermet irradiation samples has been completed and the cladding of the carbide fuel bodies is about 75% completed.

4. Studies of New Cathode Materials.

4.1 Vacuum Emission and Vaporization.

Samples of 30 UC - 70 NbC, 90 UC - 10 NbC, 30 UC - 70 TaC and 90 UC - 10 TaC have been prepared. Two 30 UC - 70 NbC samples are being outgassed prior to the studies of their rates of vaporization in vacuum.

4.2 Diffusion.

The diffusion samples of runs D_2-1, D_2-2, D_2-3 and D_2-4 have been submitted for electron microprobe studies. ZrC wafers have been

prepared for the studies of their use as barriers in the diffusion between UC and refractory metals.

4.3 Diffusion-Emission

Samples consisting of 30 UC - 70 ZrC and hypostoichiometric UC (4.70 wt-% C) clad with vapor-deposited W have been prepared for the study.

5. Fabrication Development.

Main efforts have been in the fabrication of the samples of the clad irradiation capsule.

I. EXPERIMENTAL PROGRAM.

This monthly progress report covers the work accomplished during the period April 1 to April 30, 1963, under Contract NAS 3-2532. The purpose of this contract is to continue the efforts made under Contract NAS 5-1253[1] and NAS 3-2310[2] for establishing the feasibility of UC - ZrC and the W-clad UC thermionic cathode system and to develop new cathode materials. The subjects to be studied are (1) long-term ($\geq$1000 hr) tests of the vaporization and emission stability of the UC-ZrC and the W-clad UC and UC-ZrC systems in the presence of cesium vapor; (2) studies of the controlling factors of the vaporization, emission, and mechanical properties of the UC-ZrC systems; (3) studies of the irradiation properties of the UC-ZrC and the W-clad fuel systems; (4) studies of the vaporization, emission, and diffusion properties of new cathode materials; and (5) development of fabrication techniques for controlling the structures and compositions of samples used in these studies.

1. Long-Term Tests.

1.1 Rate of Vaporization of UC-ZrC in Cesium Environment.

Previously the presence of cesium vapor at a pressure of 1.8 torr was found to reduce the rate of vaporization of a 90 UC - 10 ZrC sample A_1-1a at 2093°K by a factor of 6 during a 100-hr run[3]. During

a subsequent 100-hr run[4] with another 90 UC - 10 ZrC sample B_1-3 at 2083°K the presence of cesium vapor at 1.8 torr pressure reduced the vacuum rate of vaporization only by a factor of 1.4.

Private discussion with George Grover of Los Alamos brought out the role played by the convection current in cesium vapor in determining the vaporization loss of the carbide sample. The disagreement of the results obtained could therefore be at least partly due to the difference in the convection condition in the cell during the two runs. In a cesium cell, as the carbide cathode situates in the vicinity of an anode surface, the convection condition would certainly be different from that in the absence of the anode. The study of the effect of cesium vapor on the rate of vaporization of carbide cathodes should therefore be carried out in the presence of an anode at a temperature and an interelectrode spacing similar to that in an operating cesium cell. As the cell used for the previous measurements under this contract has no anode, main efforts during this month have been devoted to getting the two cells built during March ready to take samples. These cells are the same as the redeposition cell shown in Fig. 13 and Fig. 14 of the second quarterly report[3] and have electrode geometry similar to that in a cesium cell. The anode is cooled by water through a metal thermal barrier. By varying the thermal conductance of the barrier, the anode temperature can be adjusted from 280 to 850°C. These two cells have been assembled and outgassed. One will be loaded with a 30 UC - 70 ZrC sample of about 85 to 90% theoretical density and the other with a 90 UC - 10 ZrC sample of about the same density. The studies will be carried out first in the absence of cesium vapor with the anode at about 700 to 800°C in order to learn the anode physical redeposition effect. This will be followed by studies in the presence of cesium vapor at a pressure of about a few torr. Sample B_1-9a, whose vacuum rate of vaporization has been studied under Section 2.1, will be the 30 UC - 70 ZrC sample used for the study. The 90 UC - 10 ZrC sample has been prepared and is being outgassed.

1.2 Emission Stability of UC-ZrC and W-Clad UC and UC-ZrC in Cesium Vapor.

The operation of the second emission life-test cell (MLP-B) commenced on April 22, 1963. This cell contained the first vapor-deposited W-clad uranium carbide emitter. The cell was assembled and baked at 400°C at an internal vacuum of 5×10^{-8} torr. The sample of the geometry illustrated in Fig. 1 was inserted and the sapphire window installed. Again the cell was baked out over the week end. The emitter was then heated to various temperatures and its vacuum emission recorded. The vacuum emission values of the vapor-deposited W was in agreement with previously published data; the experimental value being $\sim$4.0 milliamps/cm^2 at 2063°K.

The cell operated for approximately five days for a total of 111 hr. For 60 of the last 70 hours of operation the cell produced a maximum power output of $\sim$2 watts/cm^2 at an emitter temperature of about 1800°C. Fig. 2 displays the performance data for two cell operating conditions. Fig. 3 is a profile of the power density for the period the cell was operating.

The cell ceased to operate on April 27, 1963. A thorough check of all instrumentation indicated that the pressure in the electron-gun portion had exceeded 1×10^{-5} torr, which tripped the ion gage relay and thus cut the cell off. A post operational attempt to reheat the cell definitely indicated a cesium leak into the electron-gun chamber. Initial analysis of the cell failure by leak checking revealed that the cell was leak-tight with respect to its ambient atmosphere, but a large leak was detected between the cell chamber and the electron-gun chamber. Further examination of the cell is continuing.

It appears that the cell has a definite problem area in the filament design of the electron-gun system. The flat pancake filament introduces considerable thermal stresses on the base of the tantalum emitter holder by concentrating most of the bombardment current in the center of the

filament. Thermal etching and grain growth in this central portion are quite evident from visual examinations of the tantalum holder. Corrective measures are being taken by several means. First, the filament will be made into a slightly conical shape with its central portion maintained at a greater distance away from the tantalum surface than its circumference. This will allow the bombardment power to be more uniformly distributed over a large surface area. Secondly, the power input for maintaining the emitter at a given temperature can be reduced by diffusion bonding the tungsten cup to the tantalum holder to provide a better heat-conduction path. Thirdly, during this diffusion bonding, a thin disc of tungsten can also be bonded to the surface of the tantalum holder facing the electron gun for thermal protection. In addition, the possibility of providing a complete tungsten holder for the emitter will not be overlooked.

There have been several other observations made during the assembly and operation of this second cell which may help to improve the cleanness and performance of future cells. During the assembly of the cell the emitter assembly must be heated to operating conditions without the collector and guard ring assembly in the system. This will eliminate the deposition of impurities from the tantalum holders, the tantalum radiation shields, and the titanium getter onto the collector surface. If any of these impurities were to form an oxide coating on the collector surface, it could introduce an electrical resistance in the cell circuit. Another area where a small electrical resistance exists, which may affect the cell output, is in the contacts between the emitter and the emitter holders. These problem areas can be checked and resolved by studying the output of a control cell containing a solid cast tungsten emitter diffusion bonded to the tantalum support tube. The emitter assembly and the collector-guard ring assembly will be outgassed separately and the diffusion bonding should help to eliminate any internal electrical resistance. Such a cell is presently being assembled. Components for the other four emission life-test cells have been received. The vapor-deposited tungsten-clad 30 UC -

70 ZrC emitters and the 30 UC - 70 ZrC and 90 UC - 10 ZrC bare carbide emitters are under preparation.

2. Studies of the High-Temperature Properties of UC - ZrC.

2.1 Effect of Porosity on the Vaporization and Electron Emission Properties of UC - ZrC in Vacuum.

Measurements have been made on the vacuum emission of the cold-pressed and sintered nominal 30 UC - 70 ZrC sample B_1-9 whose vacuum rates of vaporization have been measured during March, 1963[4]. The results are shown in Fig. 4 together with the vacuum emission data of sample B_1-7. Chemical analysis of B_1-9 after the completion of the vacuum emission measurements indicates that the sample has the stoichiometric composition 28.3 UC - 71.7 ZrC and that its density is 86.7% of the theoretical value represented by this composition. Mercury porosimeter study shows that 89% of the void in the sample consists of open pores (Fig. 5). The good agreement between the vacuum emission of B_1-9 and that of B_1-7 in Fig. 4 seems to indicate that porosity has no appreciable effect on the vacuum emission of these samples, since only 33.5% of the void in the hot-pressed sample B_1-7 (major phase 27.4 UC - 72.6 ZrC, 90% dense) consists of open pores.

Measurements have also been made on the vacuum rates of vaporization of another cold-pressed and sintered nominal 30 UC - 70 ZrC sample B_1-9a obtained from the same carbide piece as B_1-9. The results are shown in Table I and Fig. 6, together with the vacuum vaporization data of B_1-7 and B_1-9. B_1-9a will be used as the 30 UC - 70 ZrC sample under Section 1.1 for the study of the effect of cesium vapor on the rate of vaporization of UC - ZrC. Its exact chemical composition and pore structures will be determined after the cesium run.

2.2 Redeposition Studies.

To check the redeposition cell with its modified anode-cooling device, two 100-hr physical redeposition runs were made between a 1/2-in.-diameter UC cathode (1.267 cm^2 area, cold-pressed and sintered, 85% dense)

and a 5/8-in.-diameter Ni anode at a spacing of 20 mils. The first run was made at a cathode temperature of 1770°C and an anode temperature of 285°C. The cathode lost 37.2 mg and the anode captured 35.0 mg of U during this period. The second run was made at a cathode temperature of 1805°C and an anode temperature of 750°C. The higher anode temperature was realized by changing the thermal barrier of the anode cooling device from copper to stainless steel. During the 100-hr period, the cathode lost 70.0 mg while the anode captured only 33.0 mg of U. Throughout these runs, the cell and its anode cooling device behaved very satisfactorily. Systematic measurements are now being made to correlate the anode temperature with the amount of uranium capture.

2.3 Thermionic Emission Microscopy.

During this month, work has been initiated to study the activation of the emission of a UC surface in the temperature range 1670 to 2000°K in the emission microscope. The UC sample was prepared by casting and was hyperstoichiometric. Its exact composition will be determined after the completion of the study. The sample was abraded on emery paper and heated in the microscope to 1670°K. The emission pattern obtained was that typical of a polished surface, showing no structural features. Examinations made after 18 hr at this temperature revealed that the polished layer has been transformed into a heterogeneous emitting surface with well-defined bright and dark areas. Even inside the dark areas there were strongly emitting regions. The pattern remained the same after 170 hr at this temperature. The sample was then heated first to 1900°K for 12 hr and then to 2000°K for 2 hr before being brought back to 1770°K for examination of the emission pattern. An increasing amount of the surface was found to become activated after the sample was treated in this manner. It is interesting to note that each time when the sample was cooled down from a higher temperature to 1770°K, the emission pattern was dark at first, presumably due to the depletion of surface-adsorbed uranium by vaporization at the high temperature. After aging at 1770°K,

the pattern became brightened gradually until it reached the stable condition characteristic of the thermal treatment received when the surface-adsorbed uranium was replenished by diffusion. Studies of the emission pattern of this sample at temperatures higher than 1770°K, and the poisoning and regeneration of the emission are being carried out.

2.4 High-Temperature Mechanical Properties.

The high-temperature mechanical testing furnace has been assembled in the mechanical testing laboratory and thoroughly outgassed in preparation for testing of 10 UC - 90 ZrC samples. Calibration of the load train bellows has been made on the Baldwin Testing Machine. Testing on a strain-gage-instrumented steel bar with the load application rod has revealed that the measurement of the modulus of elasticity of steel by this method is a sensitive technique to establish true alignment. Difficulty has been encountered in the freezing up of the load application rod by the bearing at high temperatures. The bearing is being shifted to the cooler region to avoid this difficulty. Six 10 UC - 90 ZrC bars have been machined for the testing.

3. Irradiation Studies.

3.1 Unclad Carbide Capsule.

The irradiation of the unclad carbide capsule in GETR has proceeded satisfactorily during the second cycle. The temperature readings of the four high-temperature thermocouples during the two irradiation cycles are shown in Fig. 7*. The capsule should be back at General Atomic Hot Cell by the third week of May for post-irradiation examination.

3.2 Clad Capsule.

The cladding of the W-UC and W-UO_2 cermet samples with vapor-deposited W and machined 98 W - 2 Mo alloy has been completed and the cladding of the carbide fuels with these metals is about 75% completed. Fig. 8 shows the planned sample arrangements in the

*Although the reporting period for this report ends at April 30, 1963, the readings for May 1 to May 4, 1963, are included to give a complete picture.

four pins of this capsule. Each pin will contain one high-temperature thermocouple, located at a point where the temperature is the highest along the axis of the pin. Assembly of the capsule is expected to be finished by the middle of May, 1963, and irradiation will begin on June 15, 1963, for one reactor cycle in GETR.

4. Studies of New Cathode Materials.

4.1 Vacuum Emission and Vaporization.

UC-NbC (30-70 and 90-10) and UC-TaC (30-70 and 90-10) samples have been prepared by cold-pressing and sintering. Two 30 UC - 70 NbC samples (D_1-3 and D_1-3a) are being outgassed prior to the studies of their rates of vaporization in vacuum.

4.2 Diffusion.

A sample of 98% dense ZrC of 1/4-in. diameter is being machined to 30-mil-thick wafers to be used in the study of using ZrC as a diffusion barrier between Ta, Mo, Nb, and UC at 1800°C and between W and UC at 2000°C. The samples of runs D_2-1, D_2-2, D_2-3, and D_2-4 have been submitted for electron microprobe analysis.

4.3 Diffusion-Emission.

One vapor-deposited W-clad UC(4.70% C) and one vapor-deposited W-clad 30 UC - 70 ZrC sample has been prepared for the diffusion-emission study at 1800°C.

5. Fabrication Development.

Efforts have been devoted to the preparation of samples for the clad irradiation capsules.

II. FUTURE PLANS.

1. Long-term Tests.

1.1 Rate of Vaporization of UC-ZrC in Cesium Vapor.

Operation of the two 1000-hr test cells, one containing a 30 UC-70 ZrC sample and the other a 90 UC - 10 ZrC sample, will be initiated.

1.2 Emission Stability of UC-ZrC and W-clad UC and UC-ZrC in Cesium Vapor.

Operation of the control cell containing a W emitter will be started. Fabrication of the four life-test cells will be pursued.

2. Studies of High-Temperature Properties of UC-ZrC.

2.1 Effect of Porosity on the Rate of Vaporization and Electron Emission of UC-ZrC in Vacuum.

Efforts will be continued on the determination of the vacuum rates of vaporization and electron emission of other cold-pressed and sintered 90 UC - 10 ZrC and 30 UC - 70 ZrC samples and their pore structures.

2.2 Redeposition Studies.

Studies of the physical redeposition of UC cathode versus Ni anode will be continued in the anode temperature range 280 to 750°C.

2.3 Thermionic Emission Microscopy.

The emission patterns of UC at temperatures higher than 1770°K will be examined. The poisoning of the emitting surface by exposing to air and the regeneration of the emitting surface by thermal treatments will be studied.

2.4 High-Temperature Mechanical Properties.

The bearing guiding the loading rod will be shifted to cooler regions of the furnace and the tests of the 10 UC - 90 ZrC samples started.

3. Irradiation Studies.

3.1 Unclad Carbide Capsule.

The capsule should be back at General Atomic Hot Cell for post-irradiation examination.

3.2 Clad Capsule.

The clad capsule will be assembled and shipped to GETR.

4. Studies of New Cathode Materials.

4.1 Vacuum Emission and Vaporization.

Measurement of the rate of vaporization of 30 UC - 70 NbC in vacuum will be carried out.

4.2 Diffusion.

The microprobe results on the samples of runs D_2-1, D_2-2, D_2-3, and D_2-4 will be gathered and analyzed. The study of the diffusion between refractory metals and UC in the presence of ZrC barriers will be started.

4.3 Diffusion-Emission.

Studies will be initiated on the vapor-deposited W-clad UC and 30 UC - 70 ZrC samples.

5. Fabrication Development.

The samples for the clad capsule will be prepared. Studies of the preparation of submicron-size UC-ZrC powder will be resumed.

REFERENCES

1. Final Report for Contract NAS 5-1253, GA-3523.
2. Final Report for Contract NAS 3-2310, GA-3642.
3. Second Quarterly Report for Contract NAS 3-2532, GA-4173.
4. Monthly Report for March, 1963 for Contract NAS 3-2532, GACD-4210.

Table I

VAPOR LOSS INVESTIGATION OF 30 mol-% UC - 70 mol-% ZrC SAMPLE No. B_1-9a

Run Number	Temp. (°K)	Exposure Time (sec x 10^4)	Rate of Weight Loss ($mg/cm^2/sec$)x(10^5)	Counting Rate Alpha Counts/min/cm^2		UC Surface Concentration Based on Counting Rate (mol-%)	Density gms/cm^3
				Side 1	Side 2		
Original	-	-	-	1017	1009	16	7.67
Degas	2236	16.2	8.71	506	521	8	7.81
1	2230	6.48	4.01	470	512	8	7.85
2	2093	5.40	1.83	464	511	8	7.92
3	2138	3.96	2.13	439	473	7.5	7.92

Note:
Original composition based on chemical analysis: $U_{0.151}\ Zr_{0.367}\ C_{4.82}$

X-ray diffraction analysis performed prior to vapor-loss determinations indicated a composition of approximately 30 mol-% UC - 70 mol-% ZrC, single phase.

Based on 30 mol-% UC - 70 mol-% ZrC, the specimen was 84.7% dense prior to vapor-loss investigations.

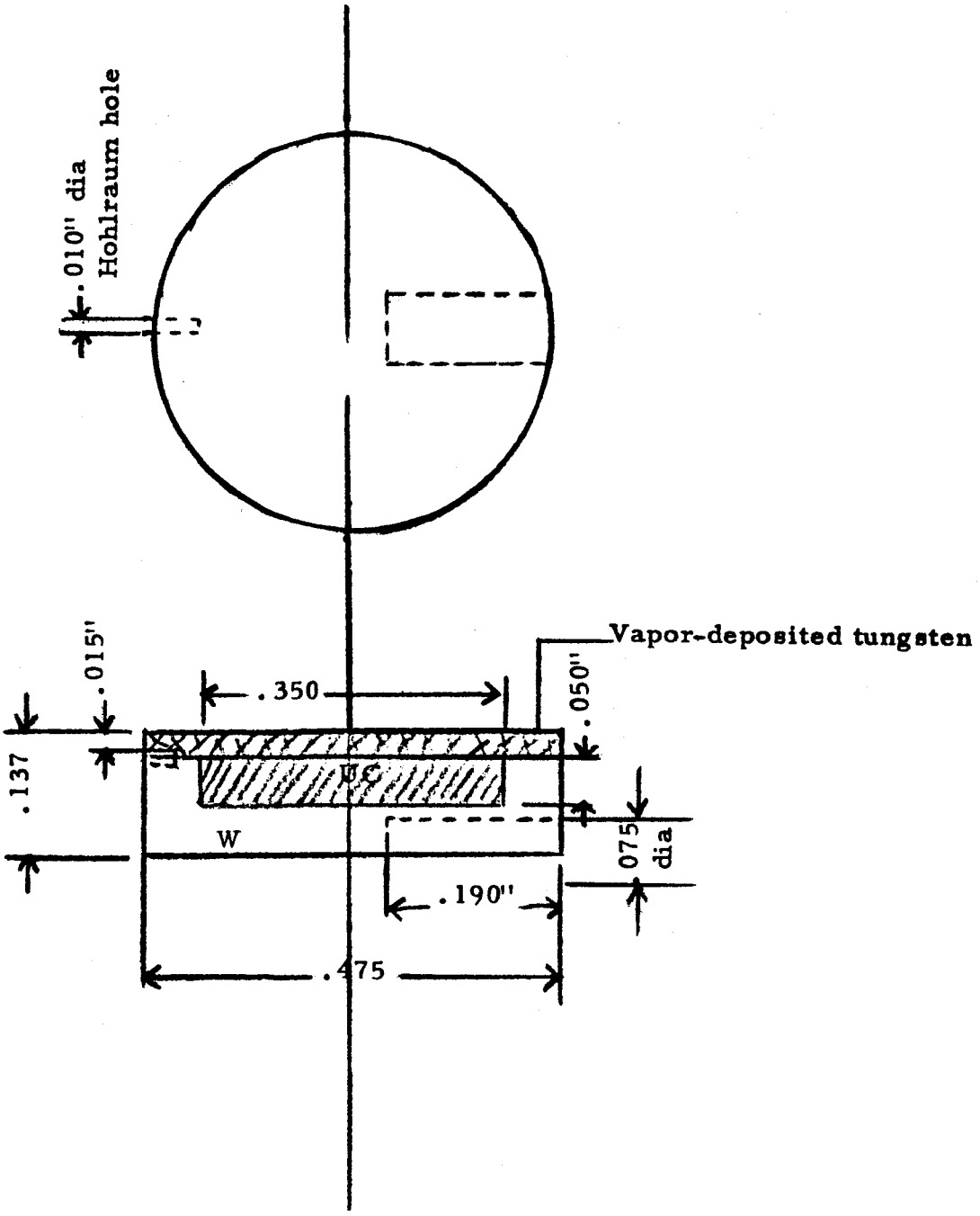

Fig. 1 --Vapor-deposited tungsten-clad uranium carbide emitter.

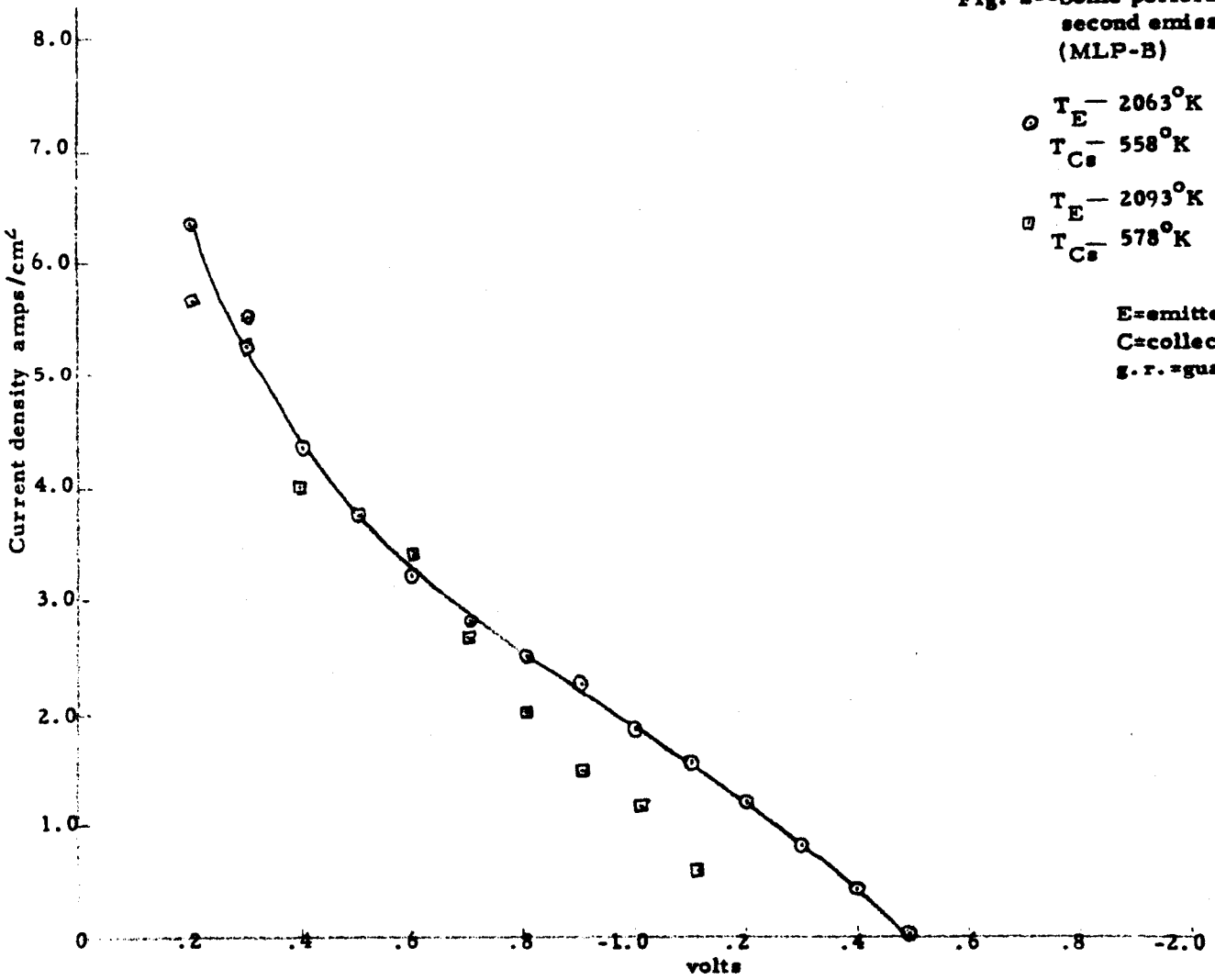

Fig. 2--Some performance data of the second emission life-test cell (MLP-B)

⊙ T_E — 2063°K T_C 995°K spacing .010 in.
T_{Cs} — 558°K $T_{g.r.}$ — 923°K

□ T_E — 2093°K T_C 878°K spacing .010 in.
T_{Cs} — 578°K $T_{g.r.}$ — 813°K

E=emitter
C=collector
g.r.=guard ring

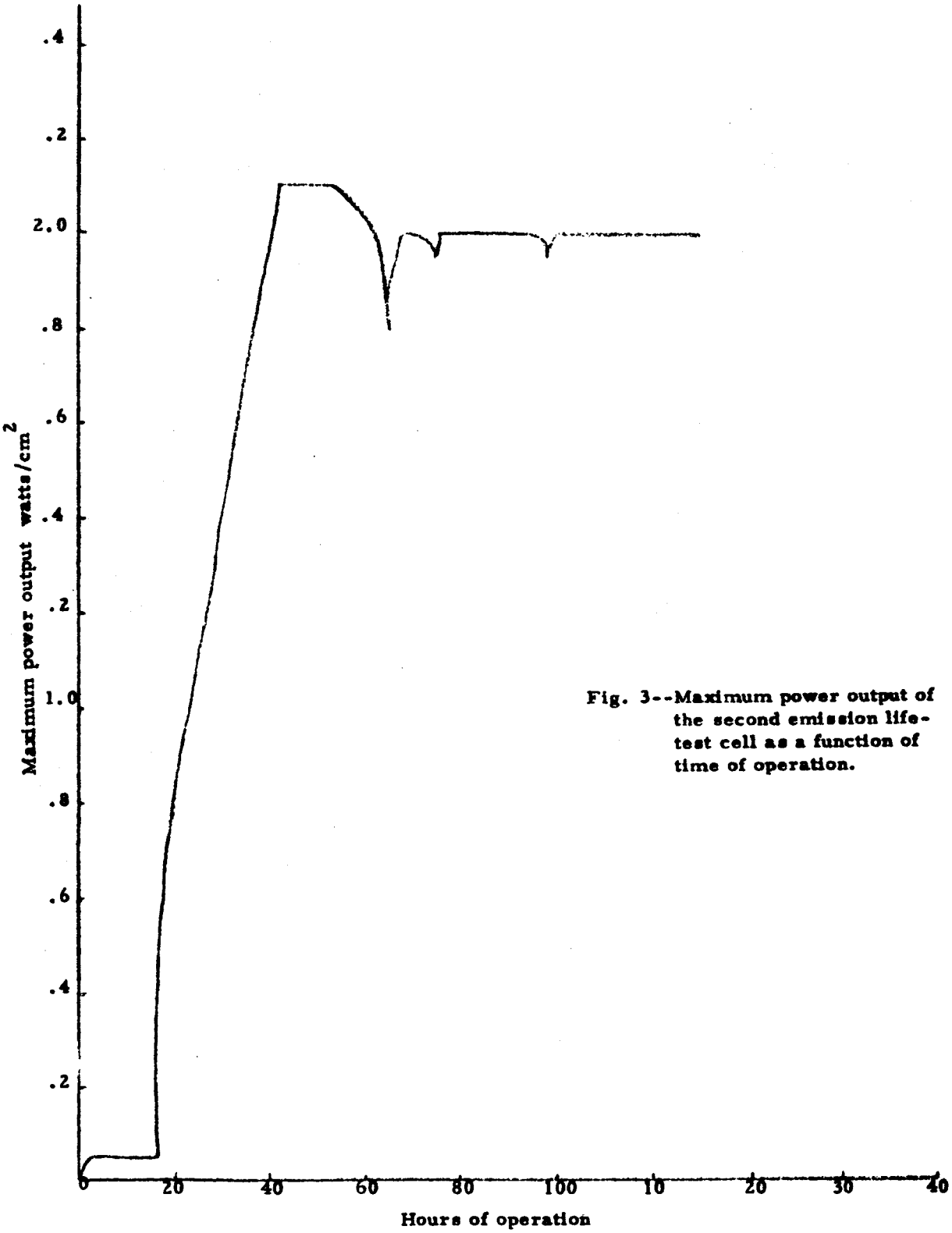

Fig. 3--Maximum power output of the second emission life-test cell as a function of time of operation.

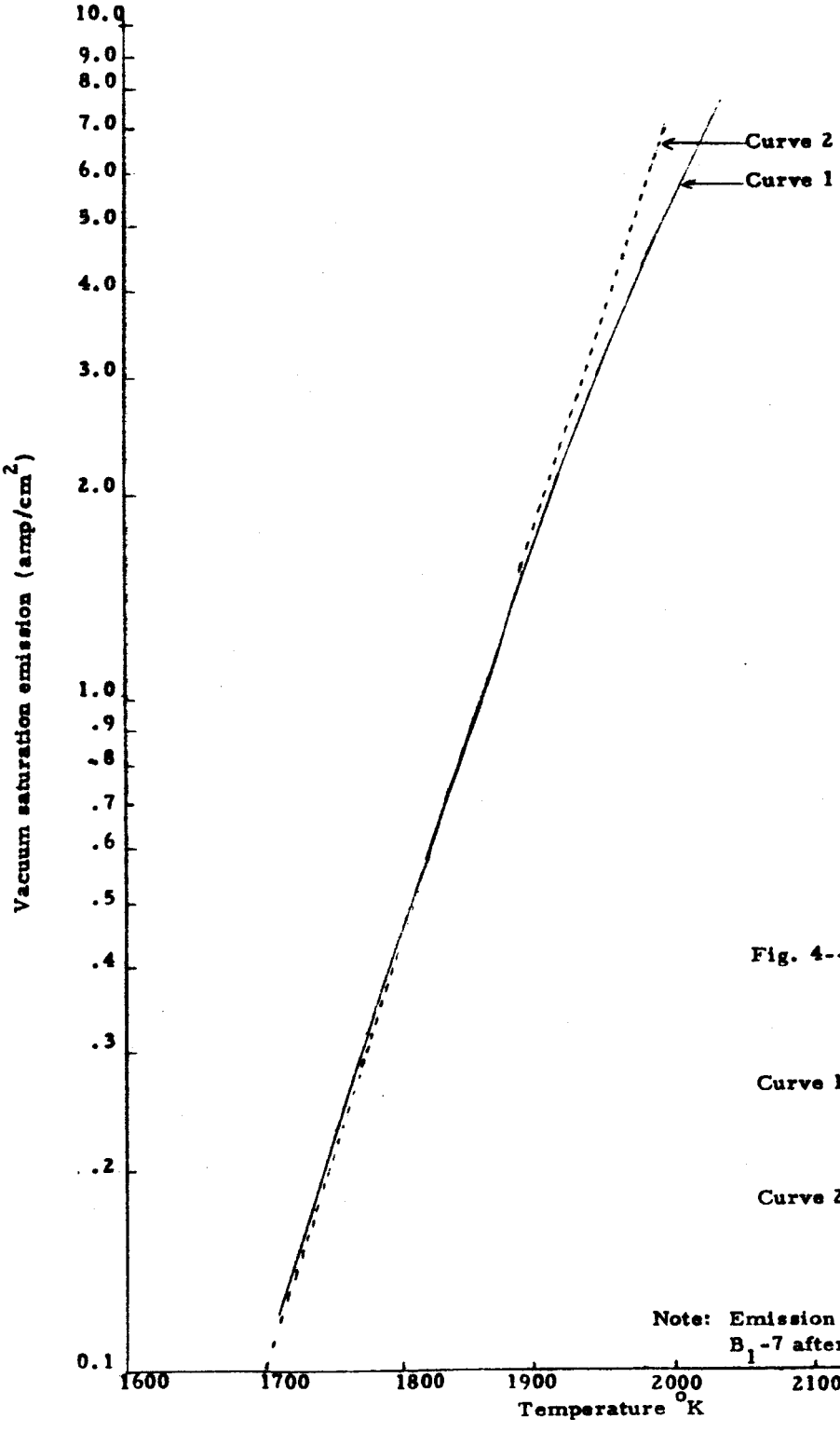

Fig. 4--Vacuum saturation emission of sample B_1-9 as compared to that of B_1-7.

Curve 1 B_1-9, cold-pressed and sintered (28.3UC-71.7ZrC, 86.7% dense, 89% open porosity).

Curve 2 B_1-7, hot pressed (27.4UC-72.6ZrC, 90% dense, 33.5% open porosity)

Note: Emission data are from B_1-9 and B_1-7 after the vaporization studies.

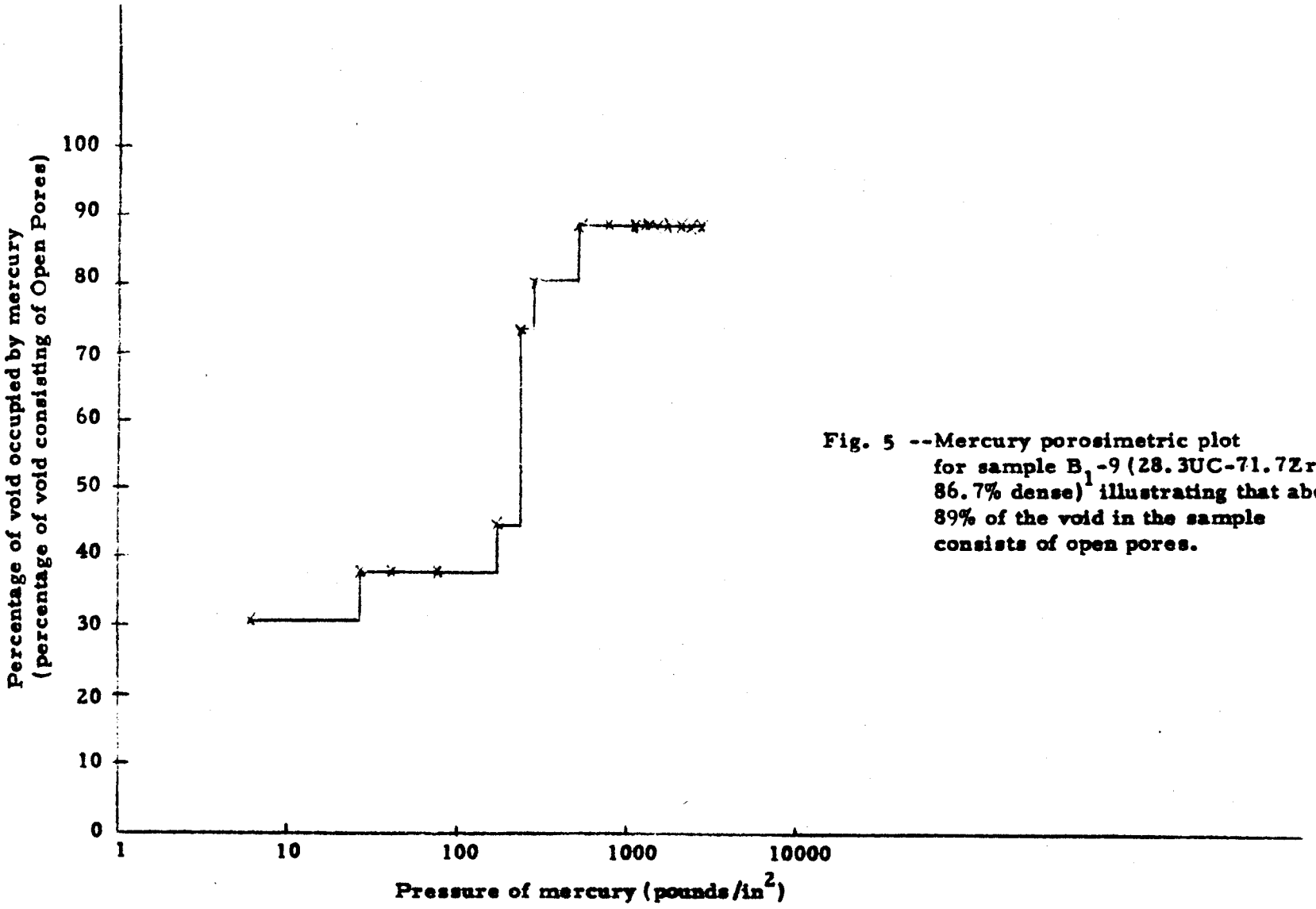

Fig. 5 --Mercury porosimetric plot for sample B_1-9 (28.3UC-71.7ZrC, 86.7% dense)[1] illustrating that about 89% of the void in the sample consists of open pores.

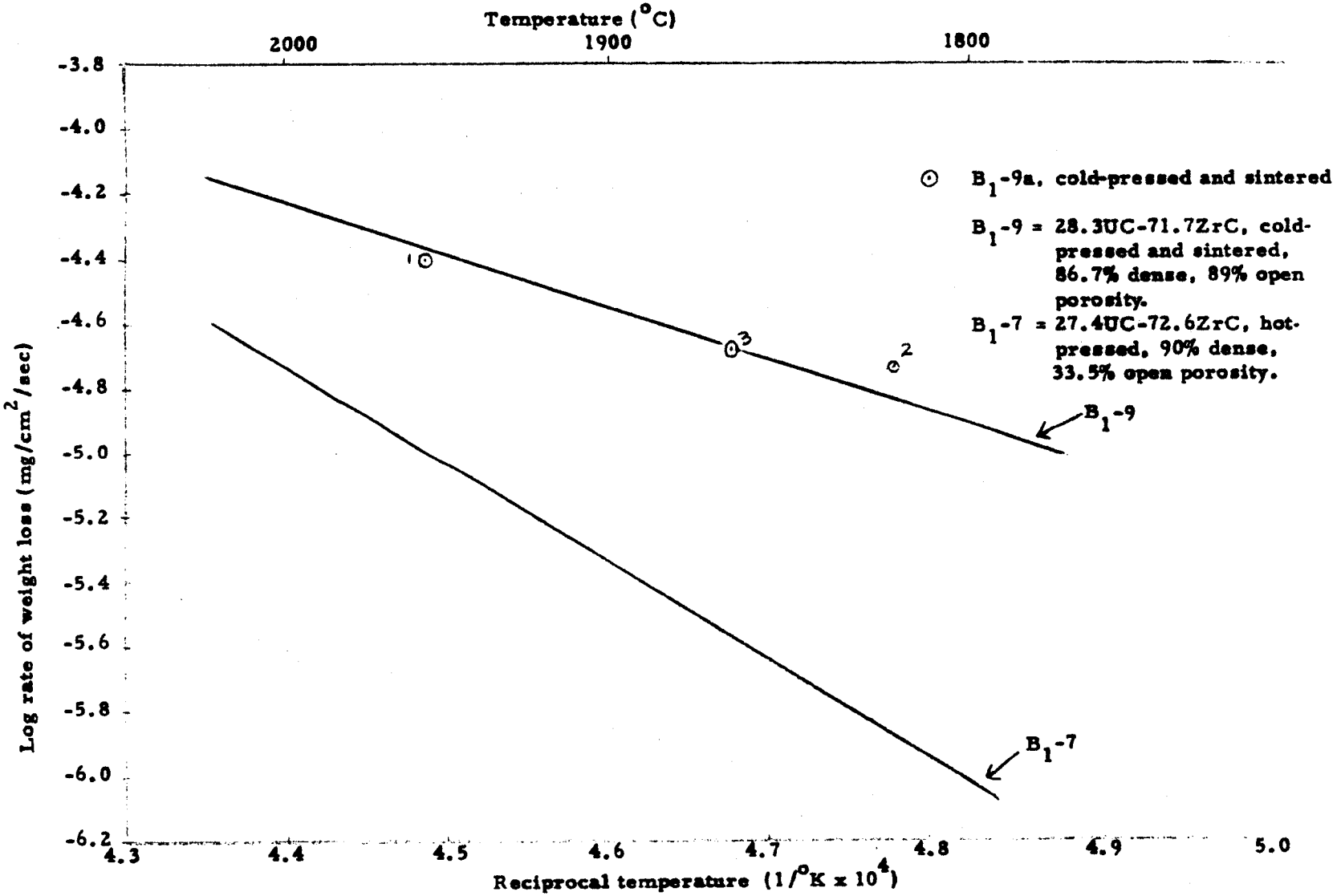

Fig. 6 --Vacuum rate of vaporization of sample B_1-9a, as compared to that of other 30 UC - 70 ZrC samples studied.
Numbers indicate sequence of runs.

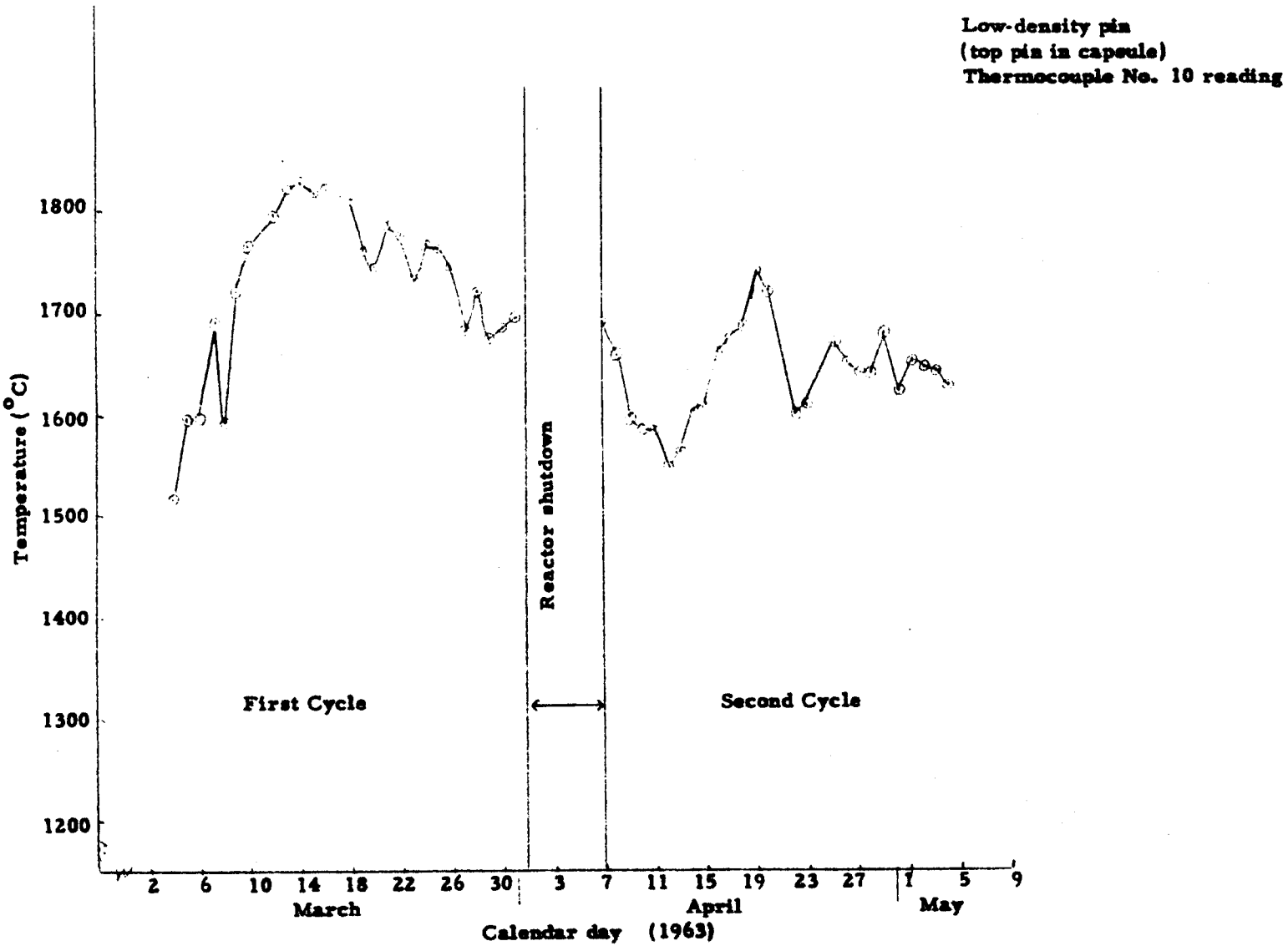

Fig. 7 --Temperatures of pins in the unclad carbide capsule GA2-306-1F1.

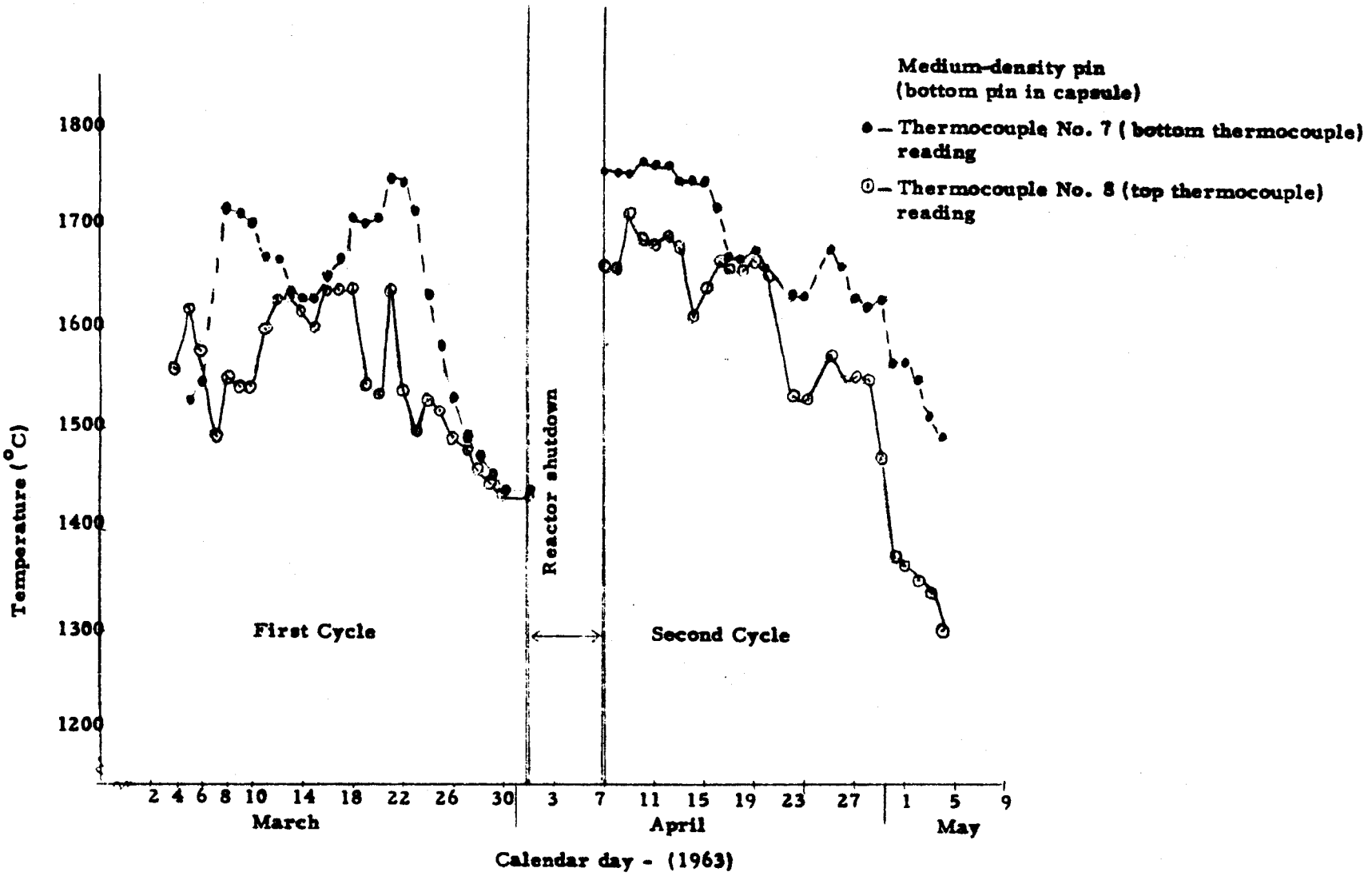

Fig. 7 --Continued

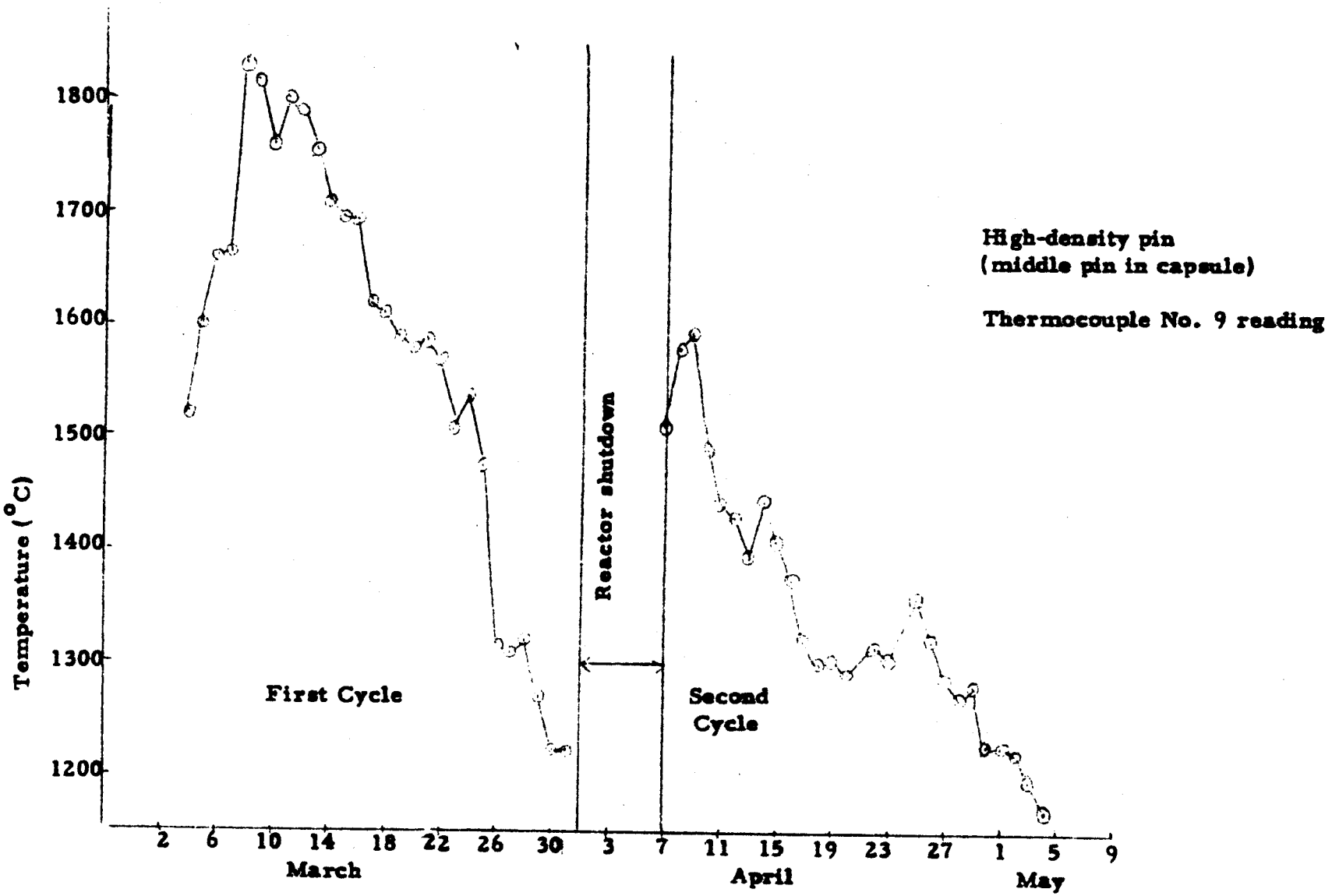

Fig. 7 --Continued.

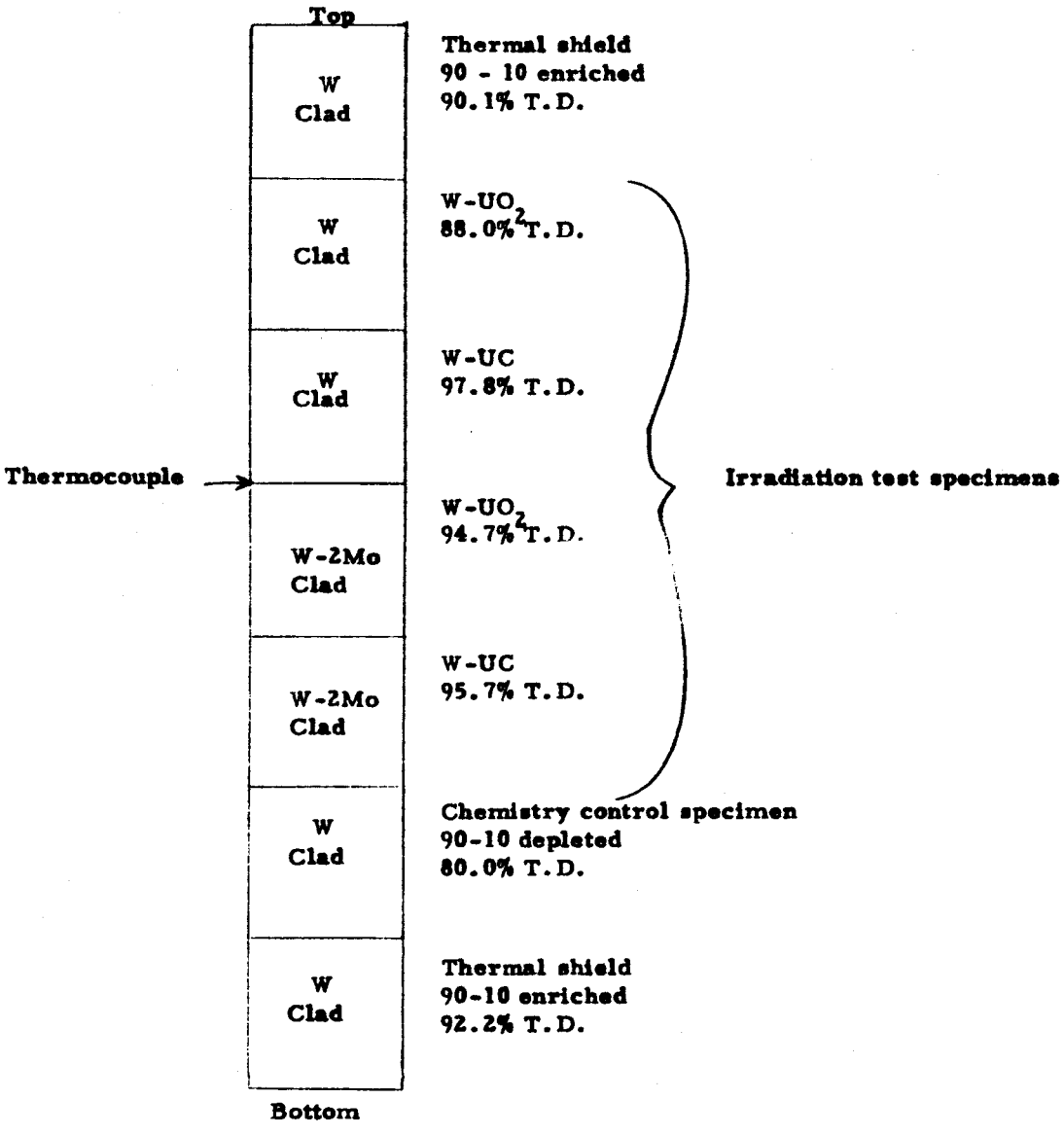

Fig. 8 --Sample arrangements in the clad irradiation capsule GA2-306-2F2.

Low-density pin (second from top)

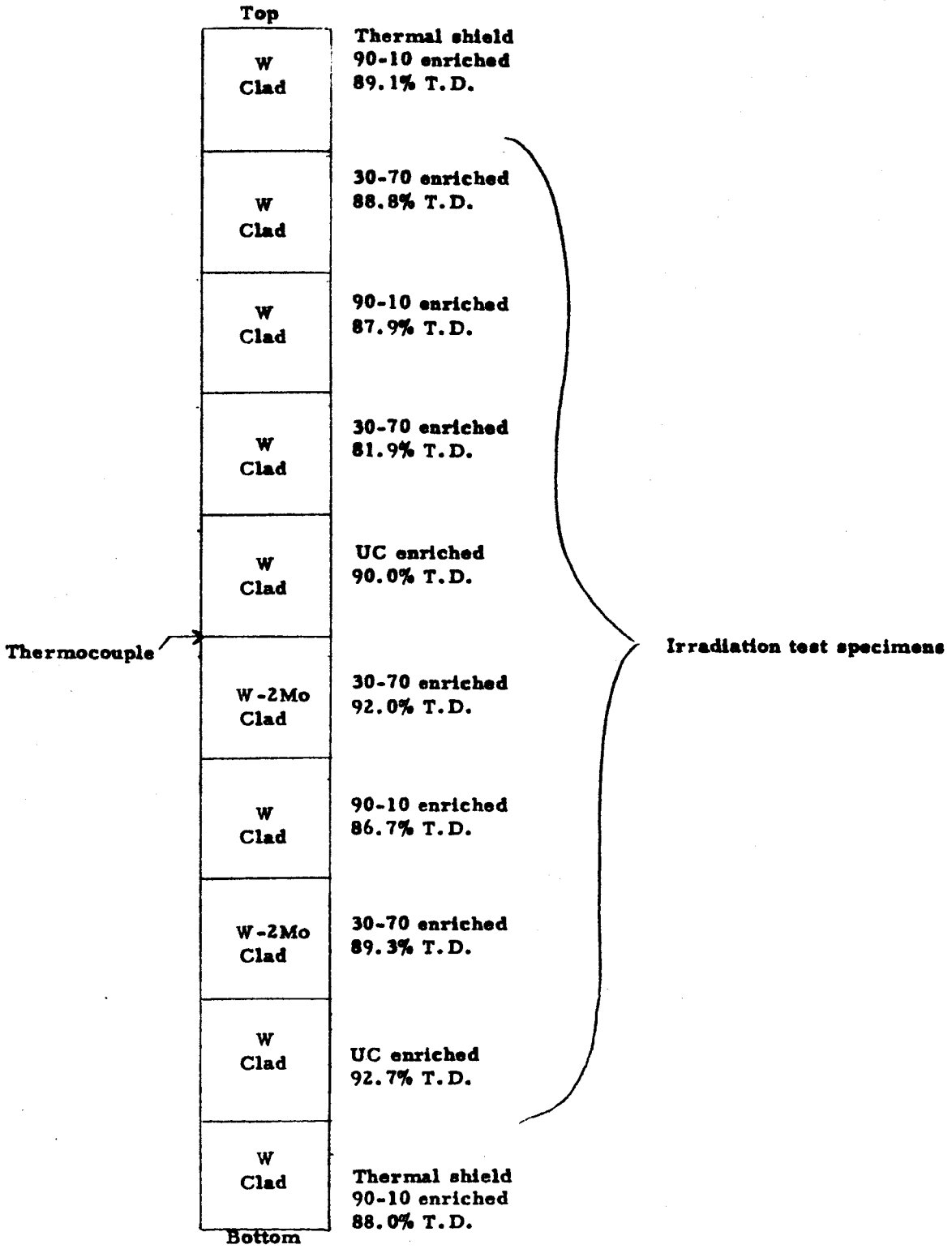

Fig. 8--Continued

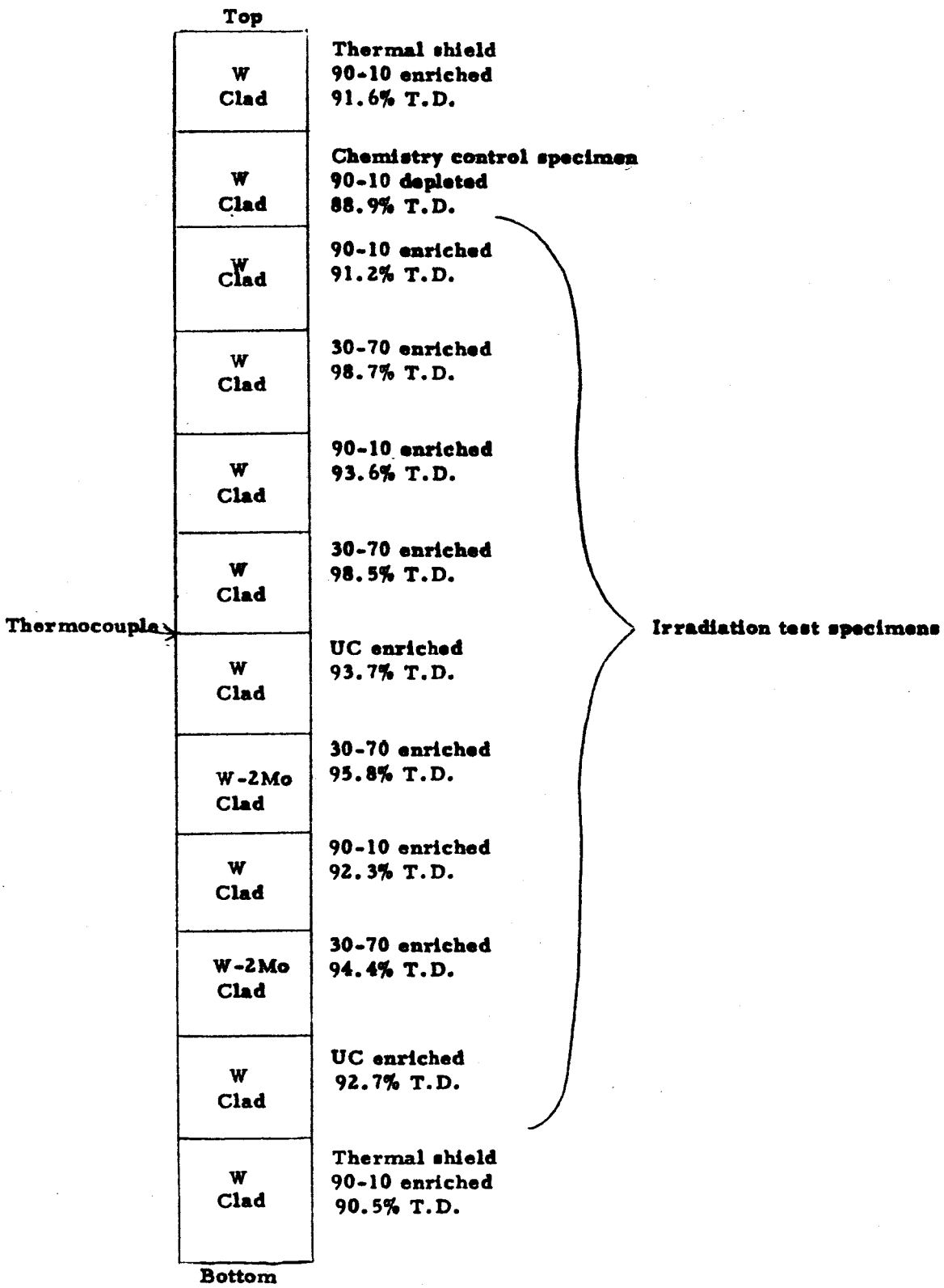

Fig. 8 --Continued

Second cermet pin (bottom of capsule)

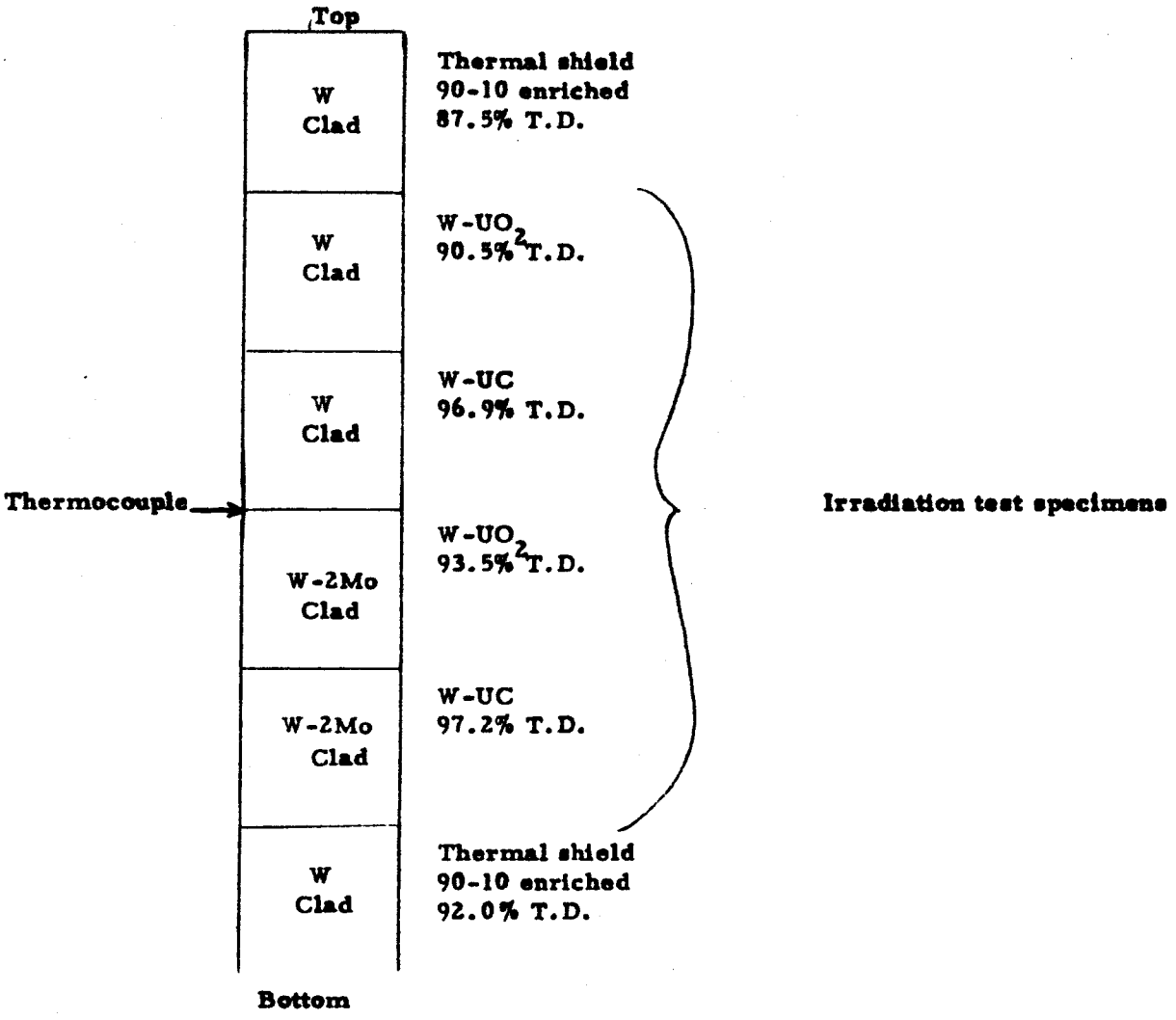

Fig. 8 --continued